

PS11.05.27 DIFFUSE X-RAY SCATTERING AND PHASE TRANSITIONS OF UREA INCLUSION COMPOUNDS. S.C. Mayo & T.R. Welberry, Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia.

Diffuse X-ray scattering studies have been carried out on the long chain alkane/urea inclusion compounds Hexadecane-Urea (HD-Urea) and 1,10-Dibromo-n-decane-Urea (DBrD-Urea). In both examples the guest species are thought to occupy the hexagonal tunnels in the host urea structure with the alkane chains able to rotate about their long axis and switch between six energetically favourable orientations. At room temperature there is thought to be very little correlation between the orientation of molecules in adjacent tunnels or (in the case of HD-urea) in their relative positions along the channels. The guests thus form a 1D crystal and this gives rise to planes of diffuse scattering normal to the tunnel direction. In the case of HD-Urea the 1D repeat is almost commensurate with the c-axis repeat of the urea framework, but for DBrD-Urea the diffuse planes occur with a repeat distance incommensurate with that of the urea.

As well as these sharp planes of scattering other distinctive diffuse scattering features are observed which are associated with the orientational ordering of the alkanes and the flexing of the urea framework. Although the diffuse scattering in these materials has been noted by other workers (see for example Harris & Thomas, 1990), the resolution of our position-sensitive detector (PSD) X-ray system has allowed us to collect high quality diffuse diffraction data at a range of different temperatures, and investigate the changes that occur as the crystals undergo a series of phase transitions at temperatures below 150K, which are thought to correspond to the orientational ordering of the alkane chains (see for example Harris, 1993). The highly structured diffuse scattering patterns have been modelled using Monte Carlo methods which simulate both the orientational ordering of the alkane chains and the flexing of the urea tunnels about them.

Harris, K.D.M. and Thomas, J.M. (1990) *J. Chem. Soc. Farad. Trans.* **86**, 2985.
Harris, K.D.M. (1993) *J. Solid State Chem.* **106**, 83.

PS11.05.28 SECOND ORDER PHASE TRANSITIONS AS STUDIED BY REAL TIME TRANSMISSION, DIFFRACTION AND SANS. G.M.Mironova, Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, 141980 Dubna, Russia

Previously^{1,2/} it was announced about the observation of the thermal shock induced phase transitions in different materials using real time neutron scattering technique developed for the last years at the IBR-2 reactor on the DN-2 diffractometer in Dubna^{3/}. Due to short accumulation of spectra (several sec for powder samples), it is possible to follow evolution of atomic structure over a momentum transfer range 0.001-10 Å⁻¹ while heating and cooling with the rates of 1-20 K/min and more. Addition of transmission channel^{4/} permits one to complete the information from the sample. Such a technique was applied for the investigation of the second order phase transitions in quartz (alpha-beta), iron (alpha-gamma) and Y-based HTSC (ortho-tetra). It was found, that all these transitions may be induced by the thermal shock, and the materials remember such events. As to phase transitions in true thermodynamical points, quite new information about scenario was received. All the data may be understood from the single point of view being controversial to modern considerations.

¹G.M.Mironova, French-Russian Seminar, Col de Porte, Grenoble, France, March 23-28, 1995.

²G.M.Mironova, A.M.Balagurov, Annual Report FLNP, 1995, Dubna.

³G.M.Mironova, Materials Science Forum v.79-82 (1991) 487.

⁴G.M.Mironova, Annual Report FLNP, 1995, Dubna.

PS11.05.29 AMMONIUM DYNAMICS AND STRUCTURAL PHASE TRANSITION IN K_{1-x}(NH₄)_xI MIXED SALTS AT 10 K. I. Natkaniec, L.S. Smirnov, Frank Laboratory of Neutron Physics, JINR, 141980 Dubna, Russia

The K_{1-x}(NH₄)_xI mixed salts have attracted increasing interest since they exhibit a low-temperature orientational glass phase. At high concentrations ($x > x_c @ 0.75$), ammonium ions are ordered as in pure NH₄I, in a slightly distorted CsCl structure of tetragonal symmetry. For $0.3 < x < x_c$, an orientational glassy phase with an antiferroelectric short range order manifest themselves in cubic structure of NaCl type [1].

We have studied the K_{1-x}(NH₄)_xI system in the entire concentration range, simultaneously by neutron diffraction and inelastic scattering (INS), on the high resolution NERA spectrometer at the IBR-2 pulsed reactor. The concentration dependence of the lattice parameters and the ammonium excitation energies at 10 K, will be presented and discussed. The energy of the torsional excitations of NH₄ vary from 36.5 meV in the ordered phase to ca. 30 meV in the disordered phase. The average energy of the translational NH₄ vibrations at ca. 20 meV, does not change significantly at phase transition and slightly increases with decreasing ammonium concentration in the disordered phase. For NH₄ concentrations below x_c, the corresponding INS spectra display two additional low energy bands at ca. 2.5 and 9 meV, while only one band at ca. 10 meV was observed in ref.[2]. Both low frequency bands reflect the localised dynamics of ammonium ions in the crystal. However, their concentration dependence is even clearer than for higher frequency modes and reflects ammonium-ammonium interactions. This implies that the C_{3v} rotational potential for NH₄ ions directly depends on such interactions. Direct ammonium-ammonium interactions contradict the presentation of this mixed salt as a pure dipolar glass [1,2].

1. J.F.Berret, C.Bostoen, B.Hennion, *Phys.Rev.* **B46** (1992) 13747-13750.
2. J. Tomkinson, B.A. Dasannacharya, P.S. Goyal and R. Chakravarthy, *J. Chem. Soc. Faraday Trans.*, **87** (1991) 3431-3433.

PS11.05.30 STRUCTURAL CHANGES IN SUCCESSIVE PHASE TRANSITIONS OF PYRIDINIUM TETRAFLUOROBORATE Takashi Nemoto, Yuji Ohashi, Minoru Hanaya and Masaharu Oguni, Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan.

Using a new diffractometer with the imaging plate, the structural changes of the successive phase transitions have been observed, although the diffraction spots were considerably splitted after the phase transitions.

The PyHBF₄ crystal undergoes first-order phase transitions at 205.2 and 238.9K (Fig. 1). The significant changes of permittivity were observed and the diffraction spots became broad and splitted after the phase transitions. The intensity data were collected using IP-Weissenberg type diffractometer. Since it was impossible to collect the splitted intensities, the new data reduction programs for the splitted spots have been developed.

The analyzed structures at three phases I, II and III indicate that both the pyridinium ion and the tetrafluoroborate ion are on the 3 symmetry at phase I (Fig. 2), the inversion centers on molecules disappear at phase II, and the a and b axes become double at phase III

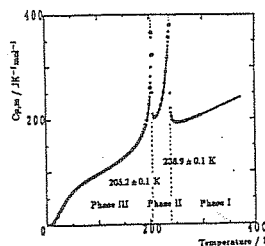


Fig. 1. Molecular heat capacity

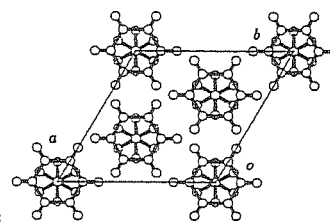


Fig. 2. Structure at 293K (Phase I)